SUPPORTING INFORMATION

Synthesis, Characterization and Atomistic Modeling of Stabilized Highly Pyrophoric $Al(BH_4)_3$ Via the Formation of the Hypersalt $K[Al(BH_4)_4]$

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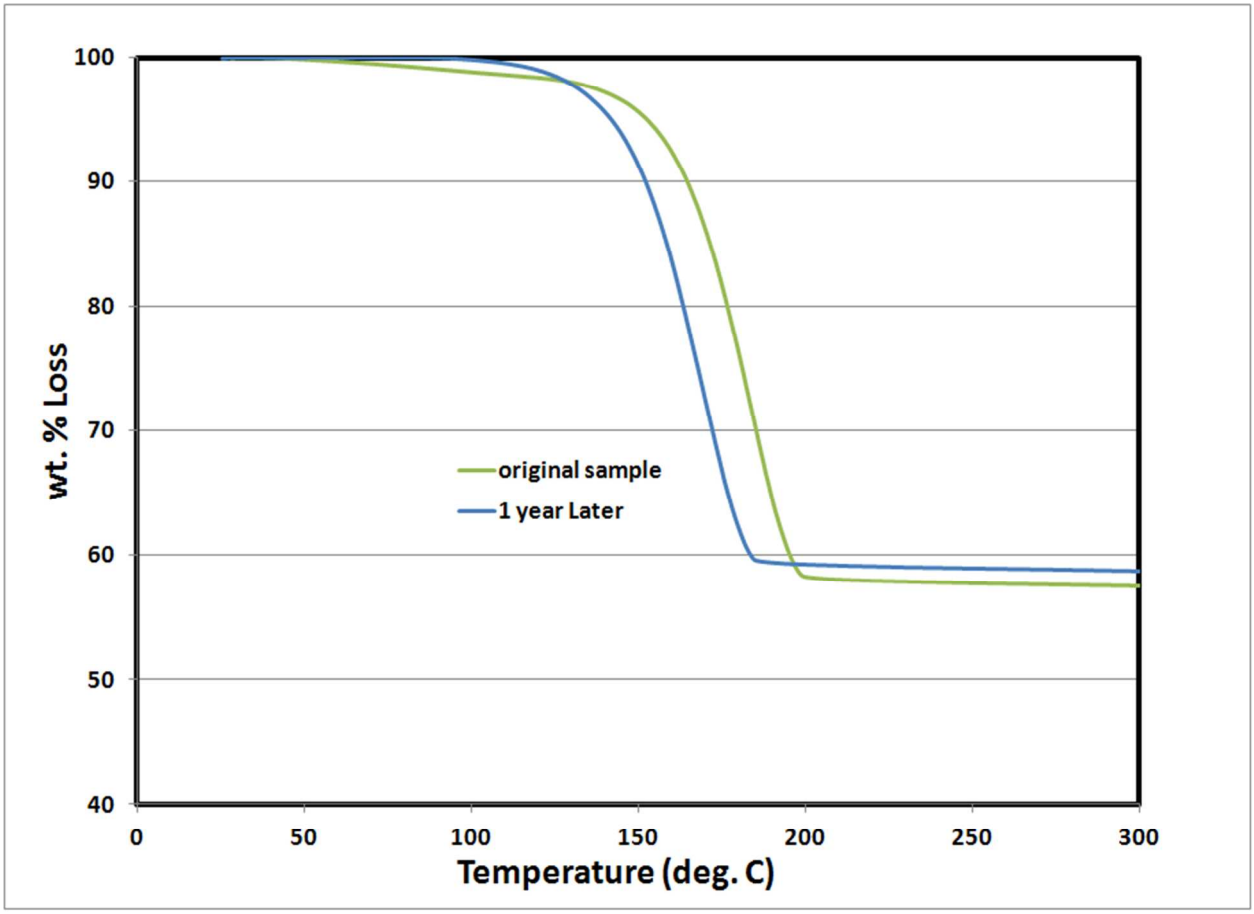

Figure S1 TGA comparison between a fresh sample of $K[Al(BH_4)_4]$ and the same sample after one year of being stored in a sealed sample vial showing there is little (if any) change in the hypersalt complex over time. The slight variance in data is within the instruments degree of uncertainty.

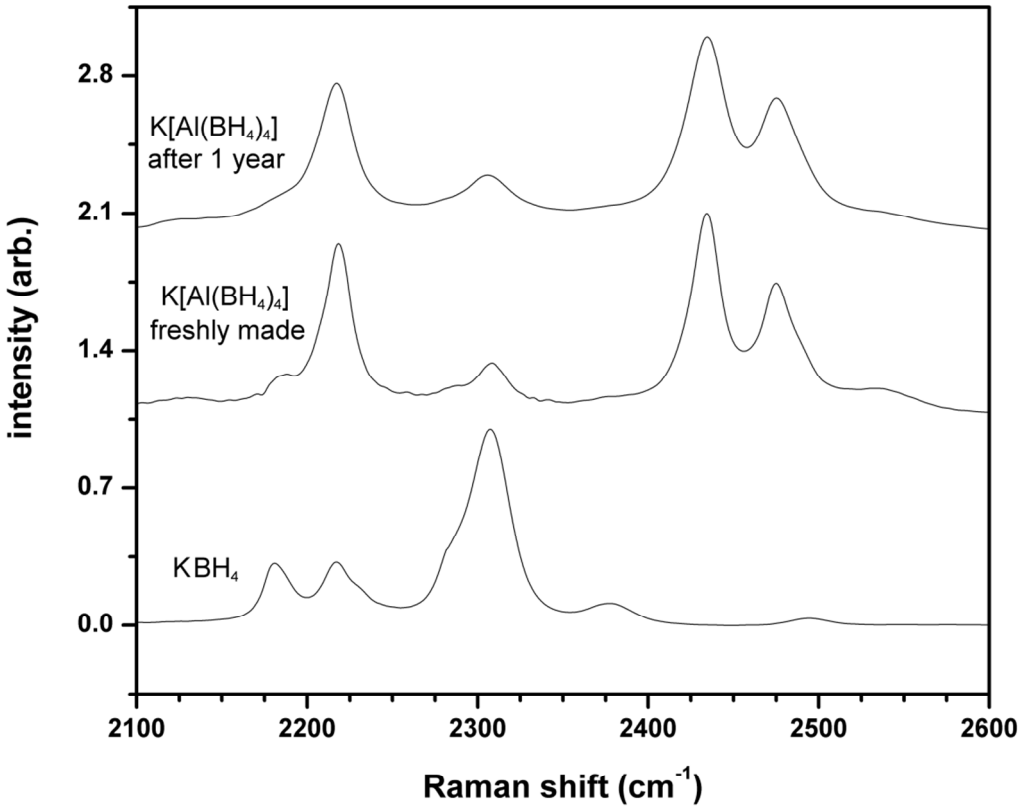

Figure 2 Raman spectra of the $K[Al(BH_4)_4]$ as it looks fresh and after storage for 1 year showing no apparent sign of material degradation. Also shown is the Raman spectrum of KBH_4.

Table S1. Optimized and Refined Structural Parameters of $KAl(BH_4)_4$
Space Group *Fdd2*, a = 9.7407(11), b = 12.4039(14), c = 14.6745(20) Å, V = 1773.0(4) Å^3

Filename	MOHT003_0	MOHT008	
Refinement	fixed VASP opt.	fixed CRYSTAL09 opt.	charge
K1, x	0	0	+0.965
y	0	0	
z	0.106033	0.091343	
Al2, x	½	½	+1.723
y	0	0	
z	0.092091	0.091062	
B3, x	0.357981	0.351518	-0.491
y	0.083825	0.066613	
z	0.189860	0.192593	
H4, x	0.247850	0.236434	-0.033
y	0.117752	0.092614	
z	0.163982	0.172499	
H5, x	0.445903	0.429222	-0.077
y	0.129261	0.120843	
z	0.141544	0.143712	
H6, x	0.359713	0.365326	-0.079
y	-0.016533	-0.030167	
z	0.180256	0.174928	
H7, x	0.388339	0.388041	+0.007
y	0.102946	0.078593	
z	0.268241	0.270079	
B8, x	0.593284	0.601343	-0.490
y	0.811283	0.816456	
z	0.740614	0.760445	
H9, x	0.671345	0.678849	-0.077
y	0.871680	0.870816	
z	0.784391	0.711519	
H10, x	0.618240	0.637722	+0.006
y	0.827800	0.828691	
z	0.661730	0.662069	
H11, x	0.477641	0.486144	-0.033
y	0.829941	0.842047	
z	0.768031	0.740285	
H12, x	0.617775	0.615633	-0.079
y	0.714092	0.719690	
z	0.754247	0.757128	

Table S2. Interatomic Distances (Å) in $KAl(BH_4)_4$

Filename			
Refinement	fixed cell VASP opt.	fixed cell CRYSTAL09 opt.	Mulliken overlap population
Al2···B3, ×2	2.248	2.235	
Al2···B8, ×2	2.264	2.235	
K1···Al2, ×2	4.875	4.870	
K1···B3, ×2	3.361	3.304	
K1···B3, ×2	3.841	3.823	
K1···B8, ×2	3.194	3.300	
K1···B8, ×2	3.824	3.824	
Al2-H5, ×2	1.837	1.822	0.064
Al2-H6, ×2	1.892	1.837	0.057
Al2-H9, ×2	1.892	1.822	0.064
Al2-H12, ×2	1.875	1.836	0.058
BVS	2.55	2.87	
K1-H7, ×2	2.608	2.724	0.000
K1-H10, ×2	2.560	2.719	0.000
K1-H11, ×2	2.751	2.834	0.002
BVS	1.43	1.29	
K1···H4, ×2	2.947	2.836	0.002
K1···H4, ×2	3.261	3.157	
K1···H11, ×2	3.186	3.156	
B3-H4	1.213	1.203	0.398
B3-H5	1.246	1.241	0.309
B3-H6	1.253	1.235	0.318
B3-H7	1.211	1.201	0.410
BVS	3.13	3.22	
B8-H9	1.246	1.241	0.309
B8-H10	1.200	1.201	0.410
B8-H11	1.218	1.203	0.398
B8-H12	1.245	1.236	0.318
BVS	3.16	3.22	

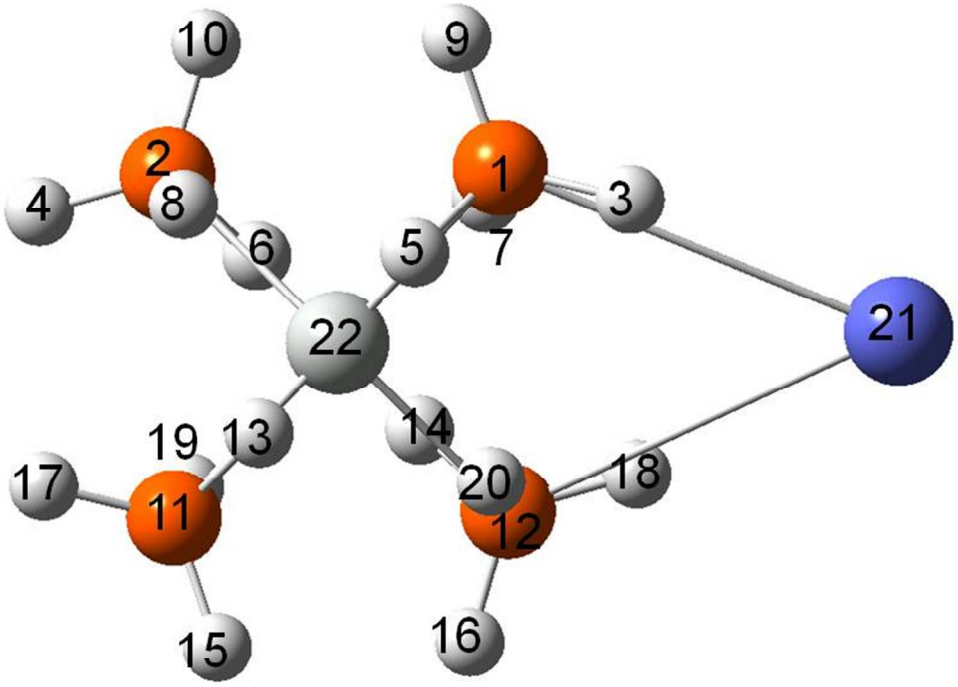

Figure S3 Structural representation of the $K[Al(BH_4)_4]$ hypersalt with numbered atoms as they relate to Table S2 containing a comparison of experimental to computational bond lengths, angles, and dihedrals.

Table S3 Comparison of computational results with experimental structural data (refer to Fig. S3)

Atom number	Atom	NA	NB	NC	Bond length		Angle		Dihedral	
					Expt.	Theo.	Expt.	Theo.	Expt.	Theo.
1	B									
2	B	1			3.331	3.352				
3	H	1	2		1.203	1.214	160.387	165.408		
4	H	2	1	3	1.203	1.196	160.387	158.616	86.236	71.065
5	H	1	2	4	1.241	1.236	74.888	73.935	-10.101	-13.120
6	H	2	1	3	1.241	1.255	74.888	74.309	-10.101	-23.847
7	H	1	2	4	1.235	1.242	54.794	59.141	118.242	114.135
8	H	2	1	3	1.235	1.253	54.794	55.103	118.242	105.900
9	H	1	2	4	1.201	1.194	78.705	79.179	-121.845	-126.224
10	H	2	1	9	1.201	1.196	78.705	79.146	30.074	28.402
11	B	2	1	9	3.406	3.503	76.118	75.045	-139.261	-140.880
12	B	11	2	1	3.333	3.352	76.102	75.021	-53.024	-55.925
13	H	11	2	1	1.241	1.255	75.929	76.865	24.619	21.043
14	H	12	11	2	1.241	1.236	74.937	73.962	-27.497	-27.801
15	H	11	2	1	1.201	1.196	152.811	152.050	-76.233	-78.894
16	H	12	11	2	1.201	1.194	78.814	79.117	-139.188	-140.930
17	H	11	2	1	1.203	1.196	85.022	84.274	132.887	129.359
18	H	12	11	2	1.203	1.214	160.234	165.494	69.048	56.570
19	H	11	2	1	1.236	1.253	49.198	48.486	-108.016	-112.330
20	H	12	11	2	1.236	1.242	54.654	59.209	100.863	99.391
21	K	1	2	11	3.823	3.123	132.107	123.836	84.110	80.338
22	Al	2	1	12	2.235	2.204	41.812	37.370	25.702	-27.968

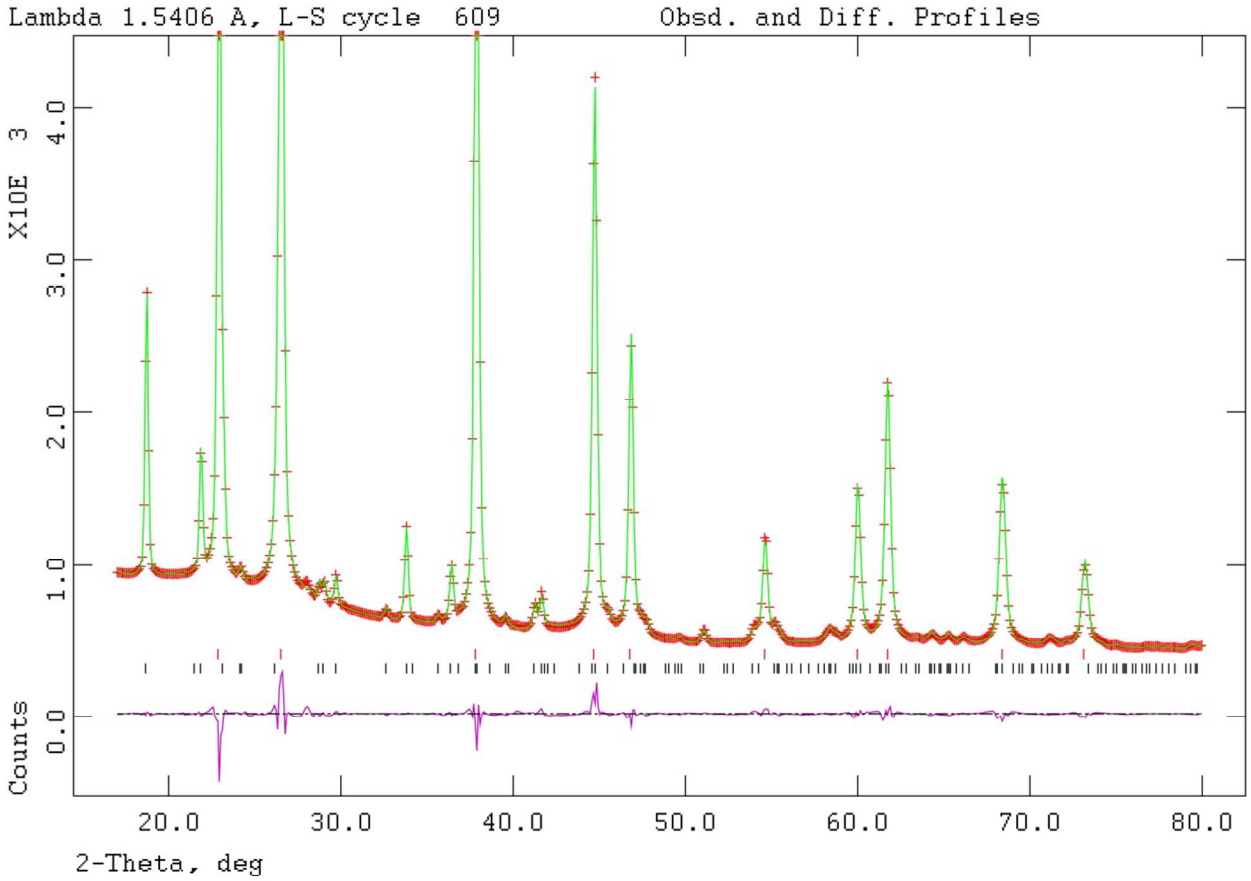

Figure 4 Calculated (green) and measured (red) Rietveld refinement plots for $KAl(BH_4)_4$. The difference plot is shown (pink).